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A new method for the kinetic study of cyclization reaction during stabilization of polyacrylonitrile fibers

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Abstract A new method for the kinetic study of cyclization reaction using the chemical shrinkage was described. The kinetic parameters derived by function fit were used to predict the rate constant at a given temperature and the feasibility of this method was verified by the Kissinger method. The results indicate that the method is feasible and the order of cyclization reaction is relevant to stabilization temperature with an activation energy of 159.11 kJ/mol.

Introduction

In processing acrylic fibers to produce carbon fiber, a stabilization treatment is crucial. The stabilization is normally carried out in the temperature range of 200–300 °C in an oxygen-containing atmosphere for adequate duration to render the fibers infusible and flameproof, and extensive research has been done in this area [1–7]. However, some important aspects are not yet well understood.

The major reaction involved in the process of stabilization is the cyclization of nitrile groups to form a ladder polymer [2]. Various authors have reported the cyclization kinetics of PAN fibers [2, 8–11]. The researchers analyze the cyclization kinetics with the *n*th-order concept by DTA or DSC, taking into consideration the peak maximum at different heating rates and the results show that the activation energy (E) varies between 100 and 180 kJ/mol. The method for the kinetic study of cyclization reaction by DSC is easy, but it could be restricted when PAN fibers are stabilized in unusual atmospheres such as ozone, sulfur dioxide, nitrogen dioxide, and so on.

When PAN fibers are subjected to heat treatment, they undergo obvious change in the length due to the cyclization and crosslinking reaction [12]. Some researchers [13, 14] have suggested that the shrinkage can be used for the in situ measurement of progressing chemical stabilization reaction. Therefore, in the present work we use the chemical shrinkage to investigate the cyclization kinetics of PAN.

Experimental

Precursors

The precursor used in this study was a commercial acrylic precursor fiber, containing itaconic acid as comonomer. The properties of the precursor are listed in Table 1.

Stabilization

The stabilization was carried out in a batch scale furnace. A fixed length of precursor fiber was tied to Kevlar thread on both its ends. For monitoring the shrinkage during stabilization, the Kevlar from one end was fixed and the other end was passed over a smooth pulley and connected to a weight, corresponding to a tension of 0.0013 cN/dTex (Fig. 1). The movement of the weight was monitored by a displacement pickup and converted to percentage shrinkage values. Results so obtained are referred to as free shrinkage, since the tension on the fibers was extremely small. Change in the Kevlar length was negligible in the

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Table 1 Properties of polyacrylonitrile fibers

Filaments in a bundle	Volume density (g cm^{-3})	Tensile strength (MPa)	Elongation (%)	Elastic modulus (GPa)	Diameter (μm)
3 K	1.180	523.6	13.36	8.12	13.33

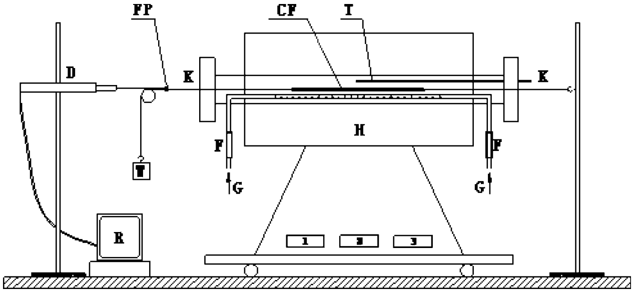

Fig. 1 Apparatus used for percentage shrinkage measurements; CF—PAN fiber, T—Thermocouple, K—Kevlar, FP—Fixed point, F—Flowmeter, G—Purge gas, D—Displacement pickup, H—3-Zone furnace, R—Paperless recorded

Table 2 Stabilization conditions of PAN fibers

Sample code	Stabilization conditions
A	30–200 °C: 2 °C/min and isothermal for 22 h
B	30–220 °C: 2 °C/min and isothermal for 22 h
C	30–240 °C: 2 °C/min and isothermal for 22 h
D	30–260 °C: 2 °C/min and isothermal for 22 h
E	30–280 °C: 2 °C/min and isothermal for 22 h

range of temperatures studied. Output from displacement pickup was amplified and noted by a paperless recorded every second. The air flow rate was 3 L/min. The stabilization conditions are listed in Table 2.

DSC

Differential scanning calorimetry (DSC) of PAN fibers was carried out on a NETZSCH STA 409 instrument. The heating rate varied between 0.5 and 10 °C/min.

Results and discussion

Kinetic study of cyclization reaction by the chemical shrinkage

The shrinkage of PAN fibers during stabilization is considered to consist of two categories: physical shrinkage and chemical shrinkage, or initial shrinkage and secondary shrinkage, and the two contributions can be clearly distinguished by a minimum in the first derivative curve [13]. The PAN homopolymer undergoes nitrile cyclization, initiated at a temperature of ~250 °C and higher. Incorporation of a small concentration of IA lowers the initiation temperature to 180–200 °C [2].

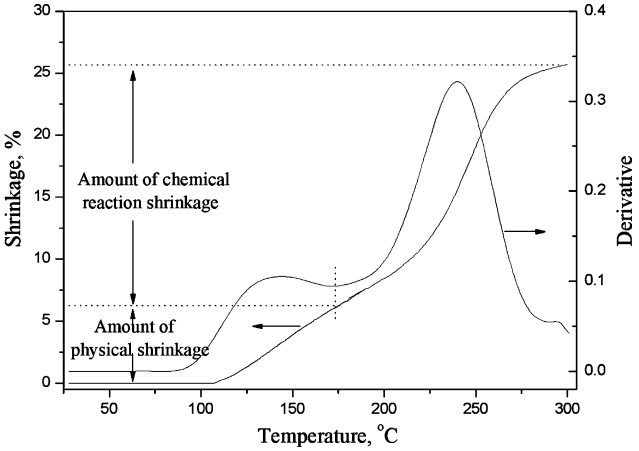

Fig. 2 Typical shrinkage curve measured during stabilization

Figure 2 shows the shrinkage of PAN fibers measured with a heating rate 2 °C/min. According to above analytical method, it is clear that the chemical shrinkage sets in ~175 °C. Therefore, the analyses of the chemical shrinkage were performed at 200, 220, 240, 260, 280 °C. Figure 3 shows the free shrinkage behavior of the PAN precursor fibers at different stabilization conditions. It is clear that the amount of the shrinkage is almost constant after isothermal for 20 h. At a given temperature, the conversion (α) at any time (t) was obtained from the relation:

$$\alpha = (S_t - S_o)/(S - S_o) \tag{1}$$

where S_o is the amount of the shrinkage when the temperature just reaches 175 °C. S_t is the amount of the shrinkage after isothermal for t hours, and S is the total amount of the shrinkage after isothermal for 22 h. The resultant conversion–time profiles and differentiate curves are shown in Figs. 4 and 5. With the increase in temperature, the initial conversion rate shows a peak at 240 °C. This is because that the reaction temperature is higher and there are more unmodified nitriles when the temperature reaches 240 °C.

The results in Fig. 5 imply that the reaction does accord with a general nth-order model. Therefore, we use a general nth-order model to fit the experimental data. For a general nth-order reaction, the kinetic expression is:

$$\mathrm{d}\alpha/\mathrm{d}t = k(1-\alpha)^n \tag{2}$$

where α is the conversion at time t and n is the reaction order and k is the kinetic rate constant. The kinetic rate

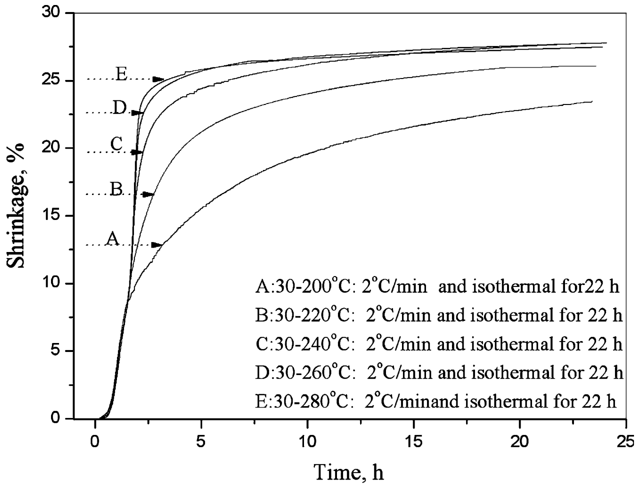

Fig. 3 Free shrinkage behaviors during stabilization of PAN fibers at different stabilization conditions

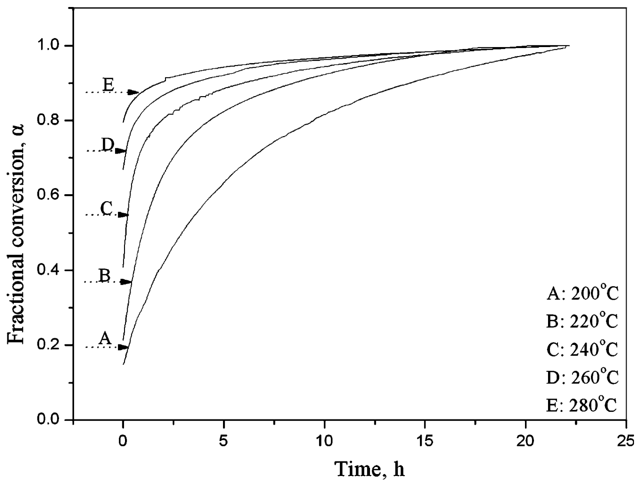

Fig. 4 Conversion–time plots at different temperatures

constant is assumed to be constant at a given temperature and to follow an Arrhenius temperature dependence, which can be expressed mathematically as follows:

$$k = A\exp(-E/RT) \tag{3}$$

where A is the pre-exponential factor, E is the activation energy, R is the gas constant, and T is the absolute temperature.

The shrinkage conversion rate curves as a function of conversion for different temperatures are shown in Fig. 6. The kinetic parameters, k and n, were calculated by fitting the experimental data to Eq. 2 for each temperature. Typical curve-fitting plots for the two cases are shown in Fig. 7. Similar acceptable curve fits were obtained in all cases, implying that the reaction conformed to an nth-order model. The kinetic parameters obtained by this method are given in Table 3. Temperature dependence of the kinetic rate constants is shown in Fig. 8, which fit quite well to form a straight line.

The order of cyclization reaction was relevant to stabilization temperature and the rate constant k increased with increasing temperature. The activation energy was 159.11 kJ/mol and the pre-exponential factor was $1.854 \times 10^{13}\ \mathrm{s}^{-1}$. The E and A values are close to the values reported by some researches [2, 8], wherein the calculations were based on DSC.

The kinetic data were used to predict the rate constants at 230 and 250 °C. According to Eqs. 2 and 3, the rate constants were calculated as 5.53×10^{-4} and $23.67 \times 10^{-4}\ \mathrm{s}^{-1}$, respectively. The chemical shrinkage at 230 and 250 °C is also investigated using the above method and the kinetic parameters obtained are also given in Table 4. It is clear that the predicted values accord with the experimental data within error limits.

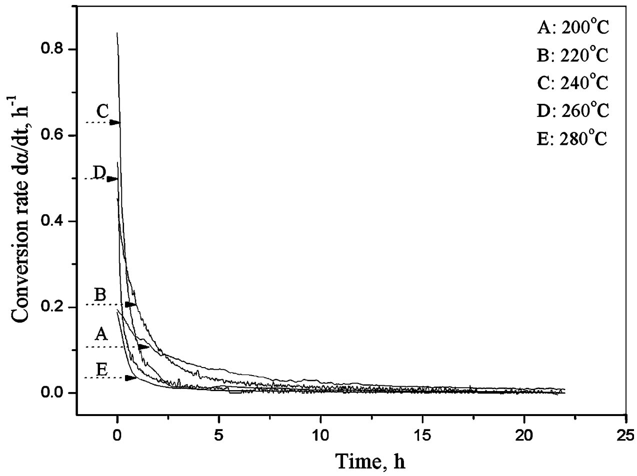

Fig. 5 Conversion rate–time plots at different temperatures

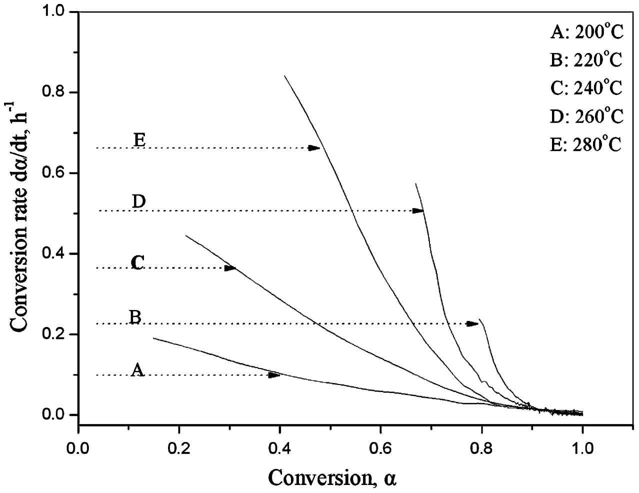

Fig. 6 Dependency of conversion rate on conversion

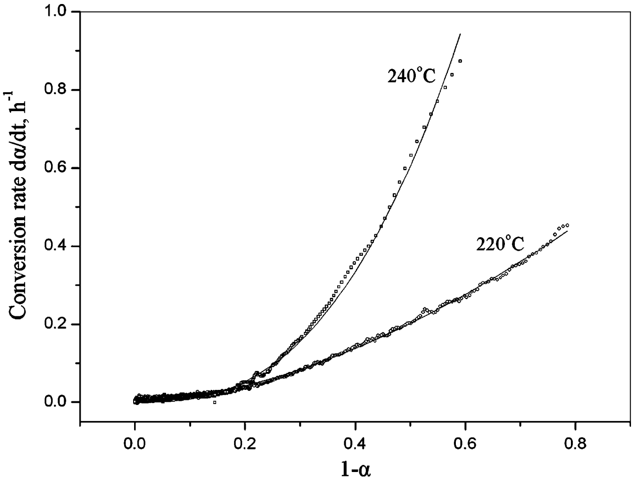

Fig. 7 Function fit for calculating kinetic parameters

Kinetic study of cyclization reaction by DSC

The activation energy E is calculated from the temperature dependence of the peak maximum T_m of the exothermic reaction in a DSC curve on the heating rate φ (°K/min) according to Kissinger method [15], as described in Eq. 4:

$$-E/R = \mathrm{d}\ln\left(\varphi/T_m^2\right)/\mathrm{d}(1/T_m) \tag{4}$$

The experimental results evaluated from DSC measurements with varied heating rates are compiled in Table 5. The peak maximum is strongly affected by the heating rate. Thus the Kissinger method can be used for evaluating activation energy.

Figure 9 shows the values of $\ln\varphi/T_m^2$ vs. $1/T_m$ calculated from the experimental data which fit quite well to form a straight line as expected from theory. Thus the maximum error is smaller than ±10% as given in literature for the Kissinger method [8]. The frequency factors k_0 can be calculated from Eq. 5:

$$\ln k_0 = \ln(E/R) + \ln\left(\varphi/T_m^2\right) + E/(RT_m). \tag{5}$$

The activation energies calculated is 158.46 kJ/mol with the frequency factor $k_0 \sim 10^{14}$. It is clear that the results calculated by the chemical shrinkage and DSC are very close. Therefore, the method that uses the chemical shrinkage to study cyclization reaction seems to be feasible.

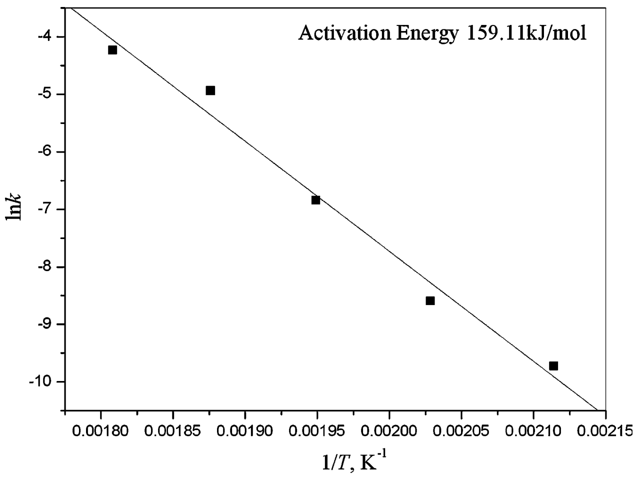

Fig. 8 Temperature dependence of k

Table 4 Kinetic parameters for cyclization of nitrile group

Temperature (°C)	$\mathrm{d}\alpha/\mathrm{d}t = k(1-\alpha)^n$, $k = A\exp(-E/RT)$		
	k ($\times 10^{-4}$ s^{-1})	n	Correlation coefficient
230	5.21	1.624	0.9958
250	26.34	2.911	0.9936

Table 5 T_m derived from DSC curves of PAN precursor stabilized with various heating rates

Heating rate (°C/min)	0.5	1	2	5	10
t_m (°C)	243.44	255.37	263.20	277.23	287.01
T_m (°K)	516.44	528.37	536.20	550.23	560.01

Conclusions

A new method for the kinetic study of the cyclization reaction by the chemical shrinkage has been proposed. The kinetics of the cyclization reaction in the temperature range

Table 3 Kinetic parameters for cyclization of nitrile group

Temperature (°C)	$\mathrm{d}\alpha/\mathrm{d}t = k(1-\alpha)^n$, $k = A\exp(-E/RT)$				
	K ($\times 10^{-4}$ s^{-1})	n	Correlation coefficient	E (kJ/mol)	A ($\times 10^{13}$ s^{-1})
200	0.594	1.318	0.9795	–	–
220	1.850	1.715	0.9946	–	–
240	10.610	2.654	0.9898	159.11	1.845
260	71.263	3.486	0.9768	–	–
280	143.570	3.418	0.9692	–	–

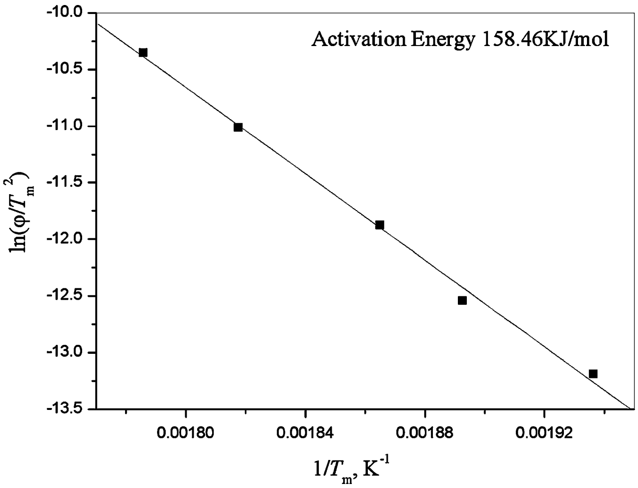

Fig. 9 Evaluation of the activation energy from DSC-peak maximum

of 200–280 °C was studied. The kinetic parameters derived by function fit were used to predict the rate constant at a given temperature and the feasibility of this was verified by the Kissinger method. The results indicated that the method was feasible and the order of cyclization reaction was relevant to stabilization temperature with an activation energy of 159.11 kJ/mol. The cyclization reaction in other atmospheres such as ozone, sulfur dioxide, and nitrogen dioxide may be studied by this method.

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References

1. Jain MK, Balasubramanian M, Desai P, Abhiraman AS (1987) J Mater Sci 22:301. doi:10.1007/BF01160585
2. Devasia R, Nair CP, Sivadasan P, Catherine BK, Ninan KN (2003) J Appl Polym Sci 88:915
3. Preta IF, Sakata SK, Garcia G, Zimmermann JP, Galembeck F, Giovedi C (2007) J Therm Anal Calorim 87(3):657
4. Pan G, Muto N, Miyayama M, Yanagida H (1992) J Mater Sci 27:3497. doi:10.1007/BF01151825
5. Kim YJ, Park CR (2005) Carbon 43:2397
6. Min BG, Sreekumar TV, Uchida T, Kumar S (2005) Carbon 43:599
7. Warner SB, Peebles LH, Uhlmann DR (1979) J Mater Sci 14:556. doi:10.1007/BF00772714
8. Fitzer E, Muller DJ (1975) Carbon 13:63
9. Ko TH, Ting HY, Lin CH (1988) J Mater Sci Lett 35:631
10. Bajaj P, Sreekumar TV, Sen K (2001) Polymer 42:1707
11. Han S, Yoon GH, Suh SK, Kim WG, Moon TJ (1999) J Polym Sci 37:713
12. Bhat GS, Cook FL, Abhiraman AS (1990) Carbon 28:377
13. Fitzer E, Frohs W, Heine M (1986) Carbon 24:387
14. Bahl OP, Manocha LM (1976) Fiber Sci Technol 9:77
15. Kissinger HE (1957) Anal Chem 29:1702